On the underlying mechanisms of the low observed nitrate selectivity in photocatalytic NO_X abatement and the importance of the oxygen reduction reaction†

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Semiconductor photocatalysis could be an effective means to combat air pollution, especially nitrogen oxides, which can be mineralized to nitrate. However, the reaction typically shows poor selectivity, releasing a number of unwanted and possibly toxic intermediates such as nitrogen dioxide. Up to now, the underlying principles that lead to this poor selectivity were not understood so a knowledge-based catalyst design for more selective materials was impossible. Herein, we present strong evidence for the slow oxygen reduction being one the causes, as the competing back-reduction of nitrate leads to the release of nitrogen dioxide. Consequently, engineering the photocatalyst for a better oxygen reduction efficiency should also increase the nitrate selectivity.

1 Introduction

Nitrogen oxides (NO_x), especially nitric oxide (NO) and nitrogen dioxide (NO_2), play a major role in atmospheric chemistry and air pollution. Despite the presence of some natural emission processes, the majority of NO_x emissions are formed anthro-pogenically in high-temperature processes such as internal combustion engines, gas- or oil-fired heating and industrial furnaces.[1] They constitute a major environmental and health concern as they are toxic compounds and also facilitate the formation of ozone and acid rain.[2,3] As a consequence, increas-ingly stronger regulations and policies are in place enforcing actions to reduce emissions and to lower the overall pollutant levels.[4] However, recent studies and events have shown that in many European cities emission standards are frequently exceeded as well as emission treatment systems not being as efficient as they are claimed to be.[5–7]

Apart from reducing the emissions directly at the emission source, which appears to be more difficult than anticipated, semiconductor photocatalysis presents an appealing alternative capable of removing NO_x and other air pollutants from the air once they have already been released and dispersed.[8] Additionally, photocatalysis needs neither maintenance nor external reagents, since the only requirements are sunlight, water and molecular oxygen, which are already present in outdoor conditions.

Nitrogen monoxide can be oxidized over illuminated titanium dioxide by hydroxyl radicals which are formed by water oxidation or by hydroperoxyl radicals, eqn (2), (3) and (10). The products of this oxidation, nitrous acid (HONO) or nitrogen dioxide (NO_2), can be further oxidized to eventually form nitric acid or nitrate ($HONO_2/NO_3$), eqn (4) and (5). The nitrate will remain on the photocatalyst until it is washed off during the next rainfall.

$$TiO_2 \xrightarrow{h\nu} e_{cb}^- + h_{vb}^+ \quad (1)$$

$$H_2O + h_{vb}^+ \rightarrow \cdot OH + H^+ \quad (2)$$

$$NO + \cdot OH \rightarrow HONO \quad (3)$$

$$HONO + \cdot OH \rightarrow NO_2 + H_2O \quad (4)$$

$$NO_2 + \cdot OH \rightarrow HONO_2 \quad (5)$$

On the other hand, the photo-generated conduction band electrons typically react with the ubiquitous molecular oxygen, forming superoxide radicals and hydroperoxyl radicals after subsequent protonation, eqn (6). The so formed hydroperoxyl radical may either take up an additional conduction band electron, eqn (7), or react with NO, eqn (10), forming hydrogen peroxide or hydroxyl radicals, respectively. In the latter case, the oxidation of NO to NO_2 constitutes two oxidation equivalents. The peroxide can subsequently be reduced in two steps to a hydroxyl radical, eqn (8), and then water, eqn (9). Hydrogen peroxide can also directly oxidize nitrogen oxides, eqn (11),

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serving as an oxidation equivalent and also releasing an addi-tional hydroxyl radical in the process. Overall, in the optimal case the reductive pathway of photocatalysis can yield up to 3 oxidation equivalents per reactive photon, effectively quadru-pling the oxidation rate. This is expected to mainly take place when the overall generation rate of charge carriers is low and the concentration of nitrogen oxides is high, so that unproduc-tive consecutive reduction events are less likely. In the worst case, molecular oxygen takes up 4 conduction band electrons to convert to water, yielding no oxidation equivalents. This high-lights the immense importance of the reductive pathway in the photocatalytic NO_x abatement.

$$O_2 + e_{cb} + H^+ - HO_2 \quad (6)$$

$$HO_2 + e_{cb} + H^+ - H_2O_2 \quad (7)$$

$$H_2O_2 + e_{cb} + H^+ - OH + H_2O \quad (8)$$

$$OH + e_{cb} + H^+ - H_2O \quad (9)$$

$$HO_2 + NO - NO_2 + OH \quad (10)$$

$$H_2O_2 + NO - HONO + OH \quad (11)$$

All of the intermediate species mentioned above, namely nitrous acid and nitrogen dioxide, may also be released during the reaction if they are not converted fast enough. This can be expressed as the nitrate selectivity of the reaction, i.e., how much of the nitrogen oxide is directly converted to nitrate and not released as intermediates. Unfortunately, this selectivity is rather low for unmodified titanium dioxide photocatalysts, which display values from only 7% to 39%, meaning that the majority is released as nitrogen dioxide instead of the desired product, nitrate.[9] This is a major problem for the targeted application as air pollution control as nitrogen dioxide is much more toxic than nitrogen monoxide, so the photocatalyst bears the potential to make the situation worse rather than better.[9] For instance, the commonly used P25 photocatalyst shows an net increase in NO_2 concentration upon being illuminated in a 1 : 1 mixture of NO and NO_2, which not untypical for environ-mental conditions, cf. Fig. S2 and S3 (ESI†). It should be noted that the selectivity is dependent on the reaction parameters, e.g., residence time, so the values are not readily transferrable to other setups.

The typical behaviour of a photocatalyst during the NO_x abatement is illustrated in Fig. 1 on the basis of Evonik Degussa Aeroxide P25 powder, it has been shown that virtually all unmodified commercial TiO_2 photocatalysts behave similarly.[9] It can be seen that the activity of the sample is quite good, almost half of the supplied NO is converted (g E 4.4 10 ^{5}), however, the main product of the reaction is not the desired nitrate but NO_2 (or HONO as the employed analyzer cannot distinguish between the two).[10–12] At the beginning of the experiment, the selectivity is already poor at approximately 32%, followed by a sharp drop to about 23% in the first hour of illumination with a continued less steep but steady decline afterwards. The absolute activity of NO conversion also decreases with time, while the NO_2 formation

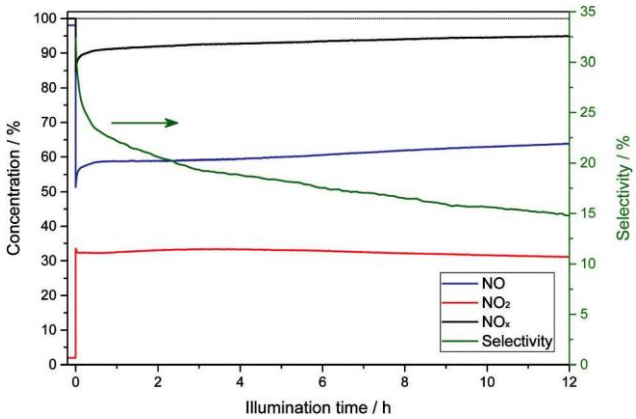

Fig. 1 A representative experiment for the photocatalytic oxidation of nitric oxide (NO) according to ISO 22197-1 using Aeroxide P25 powder. Plotted are the relative concentrations of NO (blue), NO_2 (red) and NO_x (black) on the left axis as well as the selectivity towards the desired product nitrate (green) on the right axis.

seems to be less affected by this with a barely noticeable smaller decline, resulting in the lower selectivity.

The adsorption capacity for NO_2 on TiO_2 is much higher than that for NO and should therefore buffer the NO_2 formation to some extent.[13] However, significant NO_2 evolution is usually observed immediately upon illumination. This illustrates, that there are two different mechanisms to consider. First there is the intrinsic activity of a material which is observed at the very beginning of an experiment with a clean surface. This intrinsic activity is likely governed by the individual NO and NO_2 reaction rates as well as their adsorption behaviour on the catalyst. However, if this was the only mechanism at work, the selectivity should be relatively constant in prolonged experiments. The only thing changing over time is the amount of nitrate adsorbed on the surface, which will inevitably reduce the catalyst's activity by blocking adsorption sites.

If the activity decrease was solely due to blocked surface adsorption sites by accumulated nitrate, it should affect the respective reaction rates of NO and NO_2 by the same factor, leading to an overall decrease in activity but still similar selectivity. However, in the experiments, while the rate of NO oxidation drops during prolonged experiments, the rate of NO_2 evolution stays nearly constant and is seemingly unaffected by the reduced oxidation rate of NO, which should lead to lower NO_2 formation. Also, experiments at different inlet concentra-tions of NO allow to create different ratios of NO and NO_2 reaction rates as the former shows mixed zero and first order kinetics while the latter is ideal first order. For a simple follow-up reaction one would expect the selectivity to have a strong depen-dence on the ratio between the first and second step reaction rates. However, as seen in Table S1 (ESI†), while this ratio changes from 5 to 15 with lowered inlet concentration, the observed selectivity stays virtually identical. This disconnection between NO_2 evolution rate and both the NO oxidation rate and the degree of free surface adsorption sites leads us to believe that the release of NO_2 as an intermediate species in the oxidation pathway cannot be the sole cause of the observed NO_2 evolution.

There rather seems to be an additional mechanism in place that leads to a significant decrease in selectivity in the pro-longed experiments. As essentially, the only thing changing is the concentration of accumulated nitrate on the surface, this is likely the cause for the observed phenomenon. This nitrate accumulation seems to poison the catalyst in a way that not only reduces its activity due to blocked surface sites but also reduces its selectivity. The latter effect is also much more pronounced and is noticeable at far lower nitrate coverages. In the present example with P25, the activity for NO oxidation, expressed as the apparent first order rate constant, decreases by only 0.4% from 0.894 s^{1} to 0.890 s^{1} from 1 hour to 2 hour illumination time. In the same time-frame, however, the selectivity decreases by 7.9% from 22.3% to 20.5%.

2 Proposed mechanism of the observed selectivity decline

When considering the mechanism of photocatalytic NO_x oxidation, nitrate or nitric acid is often considered to be the inert end product of the reaction which stays on the photocatalyst surface until it is eventually washed off by rain. However, there are some experi-ments which show that a nitrate-rich or nitrate-saturated photo-catalyst surface can release significant amounts of NO_2 upon illumination, even in an NO_x free atmosphere.[14] Presumably, this is caused by a photocatalytic reaction with adsorbed nitrate to nitrogen dioxide, which is subsequently desorbed and released. Previously, this has been attributed to photocatalytic oxidation of nitrate to NO_3 with subsequent photolysis, leading to NO, NO_2 and O_3.[12,14] However, in these studies NO_3 was never actually detected and it was observed that the evolution of NO_x during irradiation of a nitrate-saturated TiO_2-surface is much higher in nitrogen than in air atmosphere, which suggests that oxygen suppresses the mechanism. Also in the former case, no suitable reduction mecha-nism was reported in the absence of oxygen as an electron acceptor. Therefore, we propose here that nitrate absorbed on TiO_2 can also be photocatalytically reduced, this will directly yield NO_2 via reaction 12. We cannot say whether the previously proposed oxidation pathway via NO_3 also takes place simulta-neously, but from the strong dependence on the oxygen concen-tration we suspect the reduction pathway to be predominant. Nitrogen dioxide formed through these ''renoxification'' processes, rather than as an intermediate in the oxidation pathway, can be a major contributor of the observed nitrogen dioxide evolution during photocatalytic NO oxidation and is the likely cause for the drop in selectivity in prolonged experiments. Studies by Monge et al. have also shown HONO as a minor by-product of the renoxification, presumably formed by further reduction of NO_2.[12,14]

$$HONO_2 + e^- + H^+ \rightarrow NO_2 + H_2O \qquad (12)$$

The adsorbed nitrate on the titanium dioxide will be in constant competition with molecular oxygen for the electrons. Unfortunately, as already outlined by Gerischer and Heller in 1991, oxygen reduction on titanium dioxide proceeds slowly and will often present the rate-determining step of the overall reaction unless oxygen reduction promoting co-catalysts are employed.[15] However, if an alternative electron acceptor is present, titanium dioxide will readily reduce it. At a reduction potential of +0.80 V_{RHE},[16] nitrate is a much better electron acceptor than molecular oxygen at 0.05 V_{RHE} (one-electron-reduction).[17] Therefore, the reduction of nitrate is actually thermodynamically favoured in comparison with molecular oxygen.

Taking reaction constants obtained in stopped-flow experi-ments in liquid media as an indication, the reduction of oxygen and nitrate should proceed with similar reaction rates.[18,19] The situation in the gas phase might be different and might more closely resemble the respective redox potentials, resulting in a higher rate for nitrate than for oxygen; the following considera-tions should therefore be taken as a conservative estimate where the real behaviour might favour nitrate reduction even more. While oxygen is usually much more concentrated in ambient air than the NO_x species by 6–8 orders of magnitude, it is already enriched and immobilized on the photocatalyst surface and does not have to adsorb first. When considering the surface coverage as the rate determining element rather than the concentration in air, the situation looks much more in favour for nitrate. Ignoring the contribution of other adsorbed species such as NO, NO_2 or NO_2, since they are expected at relatively low concentrations, the surface coverage of oxygen and nitrate can be calculated using known adsorption constants for water (k_{H2O} = 50.7 m^3 mol^{1})[20] and oxygen (k_{O2} = 0.62 m^3 mol^{1})[21] and Langmuirian adsorption behaviour for competitive adsorption. The resulting surface coverage and relative reduction rate of nitrate (assuming identical reaction constants) for a model case of 50% relative humidity can be seen in Fig. 2.

Surprisingly, even at a nitrate surface coverage of only a few percent, a significant amount of electrons ends up reducing nitrate instead of oxygen. At 6.1% coverage, already a third of the electrons reduce nitrate. The diagram also shows the

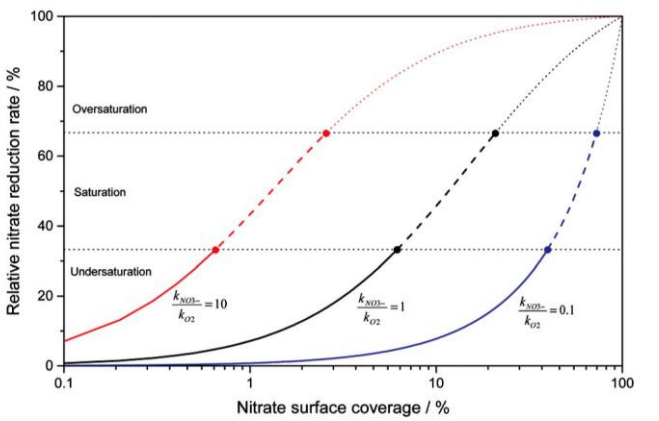

Fig. 2 The calculated relative nitrate reduction rate calculated according to eqn (23) assuming 50% relative humidity. The reaction constant for nitrate reduction is assumed to be identical (black) as well as ten times higher (red) or lower (blue) than the oxygen reduction constant, respectively. Also displayed is the expected regime for saturation if pure NO gas is used.

situation when the nitrate reduction is ten times faster than oxygen reduction, which given the redox potentials is not unrealistic, and when it is ten times smaller. In the former case, a third of the electrons reduce nitrate already at a nitrate surface coverage of 0.7% while in the latter case, it takes a coverage of 40% to achieve the same effect. A higher humidity will also further favour nitrate reduction, as adsorption sites for oxygen will be further diminished by additional adsorbed water, closely resembling the experimentally observed behaviour that the selectivity drops notably with increasing humidity.[22] Note that this calculation is neither accurate nor quantitative, as this would require presently not available precise data of the reduction constants for both nitrate and oxygen in the gas phase as well as on the competitive adsorption behaviour of nitrate, water and oxygen. This calculation can, however, give a rough estimate of the qualitative behaviour of the system and illustrate the immense importance of the oxygen reduction rate.

3 Consequences of nitrate reduction

Each electron reducing a nitrate molecule effectively neutralises one direct oxidation equivalent and up to three indirect oxida-tion equivalent by preventing the formation of a superoxide radical. Consequently, this reaction pathway is very detrimental to the overall reaction balance and should be prevented as much as possible. At some point, the chemical potential for nitrate reduction will be so high that it will completely counteract the oxidative pathway and the net nitrate concentration will be constant through the reactions (13), (6), (10), (5) and (12), resulting in the net reaction (14):

$$NO + 3h^+ + 2H_2O - NO_3 + 4H^+ \quad O_2 \qquad (13)$$

$$+ e_{cb} \quad + H^+ - HO_2 \quad NO + HO_2 \quad - \qquad (6)$$

$$NO_2 + \ OH \ NO_2 + \ OH - HONO_2 \qquad (10)$$

$$HONO_2 + e \ + H^+ - NO_2 + H_2O \qquad (5)$$

$$2NO \ þ \ O_2 \quad \overset{TiO_2\ ;hn}{!} \ 2NO_2 \qquad (14)$$

This situation will be reached when one third to two thirds of the electrons end up reducing nitrate instead of oxygen, depending on the reaction pathway, i.e., how many oxidation equivalents are generated by the reduced oxygen (0 to 3). Keep in mind that, according to our previous calculation, this can already happen at a nitrate surface coverage as low as 6% (or 0.7% if the nitrate reduction rate is ten times higher than estimated). At this point, the photocatalyst will stop reducing the overall NO_x level entirely and just turn into a very effective converter of NO to NO_2. This is exactly what is being observed when TiO_2 films are exposed NO and irradiated long enough for this equilibrium to occur. Mills and co-workers reported that TiO_2-coated glass slides show this behaviour already after a couple of hours of illumination under ISO 22197-1 conditions.[23] Similar findings were also reported by Okho et al. who observed nitrate saturation of a TiO_2 thin film after just an hour of illumination.[24]

These very thin films are naturally prone to be saturated fast as they do not have a large surface area and porosity to absorb a large amount of nitrate. Note that this situation does not represent full surface coverage with nitrate but merely a situa-tion where the formation and reduction rates of nitrate are equal. Complete nitrate coverage can be achieved by using pure NO_2 gas in the experiment, as only one oxidation equivalent (as compared to three for NO) is necessary for nitrate formation, thus keeping the balance with the corresponding electron reducing a nitrate ion. Under these conditions, roughly four times as much nitrate can be deposited onto TiO_2 when compared to using pure NO gas.[24,25] Saturation does not occur very fast with powders or thicker layers as the nitrate formed on the exposed surface can easily diff use to deeper layers which are photocatalytically inactive but serve as reservoir to dilute the nitrate coverage on the photocatalytically active exposed surface.[25] Similar eff ects can be achieved by mixing the photo-catalyst with high surface area adsorber materials such as activated carbon or cementitious matrices.[26–28] This effect will keep the effective nitrate coverage relatively constant for a long time while the reservoir is being filled, leading to the quasi-equilibrium selectivity often observed on powder samples after some irradiation time.[9] This means that for thicker samples, the nitrate surface coverage on the photocatalytically active part will be quasi-stationary for a very broad operational window where the rate of newly formed nitrate on the exposed surface is very similar to the transport to deeper layers. This will likely represent the situation in real world scenarios for most of the time and should therefore be considered for photocatalyst evaluation procedures.

If the system is artificially oversaturated, e.g. by adsorbing high amounts of nitrate on the photocatalyst prior to the experiment, it will reduce the excess nitrate under illumination and release it as NO_2 until the equilibrium is restored.[24]

The saturation situation where TiO_2 just converts NO to NO_2 (eqn (14)) is to be avoided at all costs as if it happens in real world scenarios as it will lead to an overall increase in ambient NO_2 levels. It is therefore paramount that the photocatalyst never reaches critical nitrate surface coverage in between regenerating rainfalls. This allowable period can be extended by just using a larger amount of photocatalyst or an alternative adsorber so the adsorption capacity is increased.[29,30] However, if this adsorbed nitrate in deeper layers of the adsorber can be readily washed off by rainfall and thus regenerated is not certain yet so this might only lead to a one-time eff ect that will not matter in the long term. An alternative or complementary approach is to modify the photocatalyst in a way that eff ectively suppresses the nitrate reduction pathway.

4 Suppressing the nitrate reduction

Suppressing this unwanted side-reaction could be achieved by lowering the amount of nitrate on the catalyst surface or

by making the alternative reduction reactions such as oxygen reduction more favourable. The former seems impossible to achieve as nitrate is the ultimate product of the NO_x oxidation reaction and will always be formed on an active catalyst. This leaves making the oxygen reduction more favourable in com-parison to nitrate reduction as the only viable option. This can be achieved by producing specific surface sites or employing co-catalysts which either directly improve electron transfer to oxygen or unlock the multi-electron reductions which are normally kinetically hindered on titanium dioxide. These multi-electron reductions, cf. eqn (15) and (16), feature more positive redox potentials and are thus thermodynamically favoured. The former would be more beneficial in this context as it would still generate oxidative species (H_2O_2) that could participate in the NO_x oxidation reactions.[16]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E_0 = +0.70\ V_{RHE} \qquad (15)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E_0 = +1.23\ V_{RHE} \qquad (16)$$

If the relative rate of oxygen reduction can be increased by an order of magnitude, it will have a dramatic effect on the nitrate reduction reaction, effectively suppressing it until very high nitrate surface coverages are reached, cf. Fig. 2. Also, at the same surface coverage, nitrogen dioxide release through nitrate reduction will be suppressed considerably, resulting in a significantly increased apparent selectivity. This might also explain the different selectivity of the three common titanium dioxide modifications, anatase, rutile and brookite. We recently reported that brookite (39%) is the most selective of the three, closely followed by anatase (25% to 29%), while pure rutile is very unselective (6% to 7%).[9] This can be readily explained by their different conduction band potentials, which at 0.4 V_{RHE},

0.2 V_{RHE} and 0.0 V_{RHE}, respectively, are increasingly unsuitable for oxygen reduction at 0.05 V_{RHE}.[31–33]

To prove that oxygen plays a major role in the selectivity mechanism, experiments were performed under both synthetic air (20% O_2/80% N_2) and pure oxygen atmospheres using Aeroxide P25 powders. The results for both pure NO and pure NO_2 as reactants, both in 1 ppm concentration, yielded the respective apparent first order reaction constants and the selectivity towards nitrate, cf. Table 1.

Under oxygen atmosphere the apparent rate constant for NO oxidation is increased by 55% compared to synthetic air atmo-sphere while keeping essentially the same initial selectivity. The NO_2 oxidation rate, on the other hand, is not significantly altered so that the ratio of NO to NO_2 reaction rates is increased by about 50%. This should promote accumulation of the intermediate, NO_2, and should lead to a lower observed selectivity under oxygen atmosphere, which is not observed – showing yet again that the slow follow-up reaction of NO_2 cannot be the sole reason for the observed low selectivity.

Table 1 Comparison of apparent first-order rate constants (k), reactive uptake coefficients (g) and selectivity (S) of NO and NO_2 after 2 h of reaction in both synthetic air and oxygen atmosphere. At this point, most transient effects such as adsorption have worn off while the effect of the nitrate surface coverage is still negligible (y o 0.5%)

Atmosphere	k_{NO}/s^{-1}	g_{NO}/—	k_{NO_2}/s^{-1}	g_{NO_2}/—	Ratio NO/NO_2	S/%
20% O_2/ 80% N_2	1.018	4.48 10^{-5}	0.156	8.49 10^{-6}	6.53	19.6
100% O_2	1.586	6.97 10^{-5}	0.164	8.93 10^{-6}	9.67	19.4

The nitrate surface coverage at a specific time can be calculated from the amount of formed nitrate, eqn (17):

$$y(t) = \frac{\bar{V}\,p\,A}{R\,T\,m\,S_A\,y_{max}} \int_0^t (c(NO_x)_{in}(t) - c(NO_x)_{out}(t))\,dt \qquad (17)$$

with the volume flux (V), pressure (p), Avogadro's constant (N_A), gas constant (R), absolute temperature (T), mass of catalyst (m), its specific surface area (S_A) and the maximum nitrate surface coverage (y_{max} = 2 nm $^{-2}$).[25]

Based on the idea that the nitrate reduction is the sole reason for decreasing selectivity with longer reaction times, we developed a model to describe the relationship between observed selectivity and nitrate surface coverage, eqn (18). In this equation, S_0 represents the initial or intrinsic selectivity of the sample when no nitrate is yet present, k_0 is a dimension-less figure for the relative oxygen reduction rate (cf. eqn (24)) and a is a factor that describes how soon oxygen reduction switches between four-, two- and one-electron reduction pathway. A detailed derivation of the formula is presented in Section 8.

$$S(y) = \frac{S_0}{4(y + k_0(1 - y)^3 + 3y(1 - e^{-ay/a})} \qquad (18)$$

Using this equation, selectivity-nitrate coverage profiles of different catalysts can be analysed to extract intrinsic selectivity and relative oxygen reduction rates. In order to prove the involvement of oxygen in the mechanism, experiments in both air and pure oxygen were conducted. As can be seen in Fig. 3, while the initial selectivity under both conditions is effectively identical, the selectivity drops about twice as fast with increasing

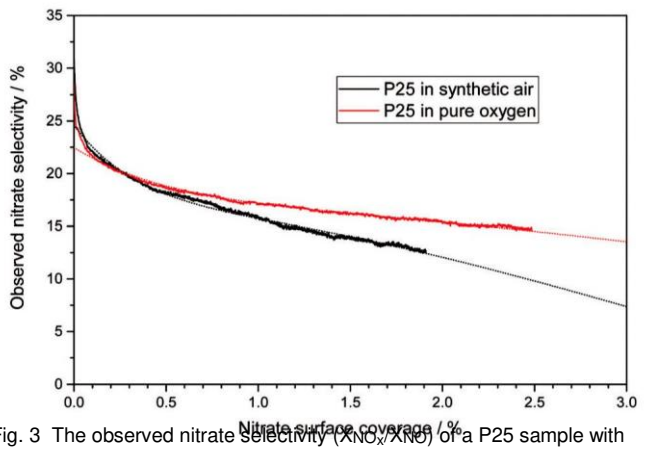

Fig. 3 The observed nitrate selectivity (χ_{NO_x}/χ_{NO}) of a P25 sample with 1 ppm NO under synthetic air (black) and pure oxygen conditions (red), plotted against the nitrate surface coverage calculated using eqn (17). Dotted lines depict the modelling according to eqn (18).

surface coverage under synthetic air compared to under oxygen atmosphere.

This illustrates that the higher oxygen reduction rate resulting from the higher oxygen partial pressure and consequently higher oxygen surface coverage mitigates the detrimental effect of increasing nitrate surface coverage on the selectivity. After an initial very fast decay, presumably caused by transient effects such as adsorption and light induced surface remodelling, the plot shows the predicted behaviour according to eqn (18) and can be fit with good precision. The resulting k_0 values are 0.095 and 0.203 for for synthetic air and oxygen atmosphere, respectively, while the intrinsic selectivity S_0 is very similar, 24.6% and 22.5%. This is a very strong indication for the involvement of the oxygen reduction reaction in the mechanism responsible for the decrease in selectivity at longer irradiation times. However, the low initial or intrinsic selectivity of the material could not be altered simply by increasing the oxygen concentration.

5 Examples of more selective catalysts

There are several reported examples of modified photocatalysts where the observed nitrate selectivity was significantly increased. These can be taken as case studies to see if the abovementioned hypothesis holds true. Keep in mind that this can either be increased selectivity from a higher intrinsic selectivity or from a higher nitrate tolerance, i.e., slower drop in selectivity with increasing illumination time. Which of the two is present is difficult to say due to the difference in employed reaction conditions.

One way to achieve a higher selectivity is by using platinum as a co-catalyst. As shown recently, the observed nitrate selec-tivity could be improved from 25% for pristine titanium dioxide to 65% by adding 0.4% of platinum to the material.[34] The oxygen reduction capabilities of the photocatalysts were not directly measured in this study, however, it is well known that platinum nanoparticles greatly enhance the oxygen reduction rate on TiO_2.[35–37] In a similar fashion, a recent study by Fujiwara et al. used palladium as a co-catalyst, another well known oxygen reduction catalyst.[36,38,39] Here, by adding 1 wt% of palladium, the nitrate selectivity was increased from 13% to up to 48% while at the same time, the absolute activity also increased significantly. However, due to their limited produc-tion and unfavorable economics, using platinum-group metals (PGM) even in sub-percent concentrations would be challen-ging for large volume applications in building materials such as concrete.

Recently, we also reported on the properties of W-doped and W/N-codoped titanium dioxide.[9,33,40,41] These materials also show dramatically enhanced selectivity towards nitrate of more than 80% when doped with a least 4.8 at% of tungsten. Unfortunately, this beneficial property comes at the expense of absolute NO_x abatement activity, which in turn decreases by a factor of 4. The increased selectivity is also accompanied by improved oxygen reduction capabilities as determined by oxygen reduction current measurements.[42] Interestingly, these materials do not seem to evolve any nitrous gases when a nitrate-saturated sample is exposed to UV radiation. This is further evidence for the theory that enhanced oxygen reduction suppresses competitive nitrate reduction which in turn leads to higher observed selectivity.

The same procedure can also be applied to other semi-conductors. We recently reported several studies on zinc oxide for NO_x abatement.[43,44] While zinc oxide seems to be more selective intrinsically, showing 55% nitrate selectivity as a pristine material, it can be further improved by decorating the particles with transition metals that facilitate the oxygen reduction reaction.[44] The selectivity is increased from 55% to 87% by just adding 0.1 at% of ruthenium.[44] Higher concentra-tions of the metal do not further increase activity or selectivity. Interestingly, while the conversion of NO is decreased for the ruthenium-modified samples, owing to the higher selectivity, the overall conversion of NO_x is slightly increased.[44] These changes are accompanied by an increased oxygen-reduction capability, which is increased by the factor of 14 in comparison to pristine ZnO.[44] Another example is manganese-modified zinc oxide.[43,44] These materials exhibit very high selectivity towards nitrate of 85% or higher when modified with at least 1 at% of manganese.[45] The selectivity increase is accompanied by a dramatic increase in oxygen reduction capability, as seen in oxygen reduction current measurements.[44,45] Both, the onset of oxygen reduction is shifted anodically, indicating multi-electron-reduction, as well as the current is higher than in pristine zinc oxide by a factor of up to ten. However, as in the case of W-doped TiO_2, the absolute NO_x-abatement activity of the samples is lowered when compared to pristine ZnO by a factor of 4.[45]

Up to now, more selective DeNOx photocatalysts have either utilized very expensive metal co-catalysts (Pt, Pd, Ru) or the selectivity increase was accompanied by a reduction in absolute activity (Mn-modified ZnO, W-doped TiO_2). The former are unsuitable for the large-scale application in building materials as even using very low amounts of noble metals will increase the catalysts price by several orders of magnitude. The latter might be suitable for large-scale application but their lowered activity will reduce the overall efficacy of the material.

While we do not yet have definite proof of the proposed mechanism of increased selectivity, all experimental evidence gathered, both by ourselves and independently by other groups, points towards enhanced oxygen reduction being the cause of the increased selectivity. If this is the case, it can be achieved with far easier means than the previously mentioned examples.

It is well known that grafting a photocatalyst with transition metal ions such as Cu^{2+} or Fe^{3+} significantly increases their oxygen reduction capabilities.[46–48] The grafting can easily be achieved with wet impregnation techniques and only uses very small amounts of abundant and affordable elements. As an additional benefit, the modification is usually accompanied by an increase in observed activity due to the enhanced charge separation and as a direct result of improved oxygen reduction as well as a slight visible light activity. If our theory holds true,

these materials should also exhibit higher nitrate selectivity in NO_x abatement experiments, while avoiding all the negative side-effects of the previously mentioned approaches.

6 Conclusion

The nitrate that is formed during the photocatalytic NO_x abatement is not just a non-reactive end-product but leads to nitrate poisoning of the catalyst, resulting in lower activity but more significantly, in greatly reduced selectivity. The latter is likely a result from the back-reduction of nitrate, a competitive reaction to the reduction of molecular oxygen.

This unwanted and extremely detrimental reaction can be effectively suppressed by making the oxygen reduction more favorable in comparison, e.g., by increasing the oxygen partial pressure or by modifying the photocatalyst with oxygen-reduction co-catalysts. An analysis of reports of more selective photocatalysts revealed that all of them have improved oxygen-reduction capabilities, as well.

If this is done in a controlled way that does not compromise the intrinsic photocatalytic activity of the material, such as selectively doping or grafting the surface with a very small concentration of co-catalysts, the increased selectivity could probably be achieved without any negative side-effects. Consequently, these materials would be much better suited for the application in building materials for environmental air pollution reduction and should replace the currently employed first-generation photocatalysts.

Also, research should be devoted to determining the expected duration the photocatalyst will experience in the field between regenerating rainfalls and the amount of nitrate surface coverage that is achieved in that interval. This state will ultimately represent the real world working conditions and this presently lacking information will help to further optimize the catalyst with respect to minimizing its nitrogen dioxide forming potential. Evaluation of photocatalyst materials in the laboratory, which are at present usually performed on freshly prepared nitrate-free materials, should also be done at nitrate surface saturation conditions that better resemble expected real world scenarios.

7 Experimental details

The NO_x abatement experiments were performed in a setup according to the international standard ISO 22197-1.[49] The nitrogen oxide gas, either nitrogen monoxide or dioxide, was supplied as a concentrated test gas mixture and was diluted to 1 ppm and 3 L min ^{1} flow rate by both a dry and wet synthetic air steam and made up to 50% relative humidity. This test gas mixture was then passed through the photocatalytic reactor made out of PEEK which comprises a sample holder with the dimensions of 5 10 cm^2, in which the photocatalyst powder was placed. Approximately 2.8 g of the photocatalyst powders were uniformly dispersed on the sample holder and slightly pressed on with a flat plunger to form a uniform flat surface. The sample holder is illuminated from above through a UVA transparent cover glass by a 365 nm UVA-LED-array (Omicron Laserage Laserprodukte GmbH, Germany) which is calibrated to deliver an irradiance of 10 W m ^{2} at the sample surface. The gas steam is passed above the sample through a 5 mm high slit that is regularly reduced to 1 mm by turbulence barriers, which was reported to improve mass transfer (see Ifang et al. for details).[50] All tubing and connections were made of polymers to avoid metal surfaces which could catalytically convert the NO_x. The resulting gas steam was analyzed using an environmental NO_x analyzer (Horiba APNA-370). It should be noted that the used analyzer does not discriminate between HONO and NO_2 but measures both as NO_2. Consequently, all values reported herein for NO_x are strictly speaking NO_y.

The changes in the concentrations of the pollutants were used to calculate the conversions ($X = 1 - c/c_0$) and the nitrate selectivity $S = \frac{X_{NO}}{X_{NO}}$. From these, apparent first order rate constants were calculated according to eqn (19).[50]

$$k = \frac{\ln(c/c_0)}{t} \quad (19)$$

Since the residence time (t) in the reactor is 0.5 s, the formula can be rewritten as eqn (20).

$$k = 2 \ln(1 - X)\ s^{-1} \quad (20)$$

In order to make the data more comparable and setup-independent, reactive uptake coefficients (g) have been calculated according to eqn (21), with a surface-to-volume ratio (S/V) of 200 m ^{1} for the ISO setup.[50] Factors for converting rate constants into reactive uptake coefficients for the given system are 4.397 10 ^{5} s for NO and 5.445 10 ^{5} s for NO_2, respectively.

$$g = \frac{4\ k}{v\ S/V} \quad (21)$$

It should be noted that the kinetic constants for NO oxida-tion determined this way are imprecise and likely significantly underestimated. The reason for this is twofold. First, for the given system the the kinetics are not ideal first order but mixed first and zero order, cf. Fig. S1 (ESI†). Also, for the high conversion values observed, the reaction is significantly influ-enced by mass transfer.[23] Therefore, the data are reported as apparent first order kinetic constants and should only be taken as a lower limit, the real values are likely significantly higher. Unfortunately, an accurate determination of the kinetic con-stants would require both very low pollutant gas concentration and significantly lowered light intensity to achieve both ideal first order kinetics and a low conversion. This negatively impacts the precision of the measurement but more importantly, makes the results not readily transferable to ISO conditions, under which most reported experiments are performed. We therefore chose this imprecise approach in order to retain comparability with the majority of the literature.

The above limitation does not hold true for the case of NO_2, which shows ideal first order behavior in the concentration range studied and also shows low conversion which should not be significantly influenced by mass transfer limitations.

8 Model derivation

The surface coverage of oxygen (y_{O_2}) as a function of nitrate surface coverage (y_{NO_3}) and relative humidity (k_{H_2O}) can be calculated according to eqn (22) using Langmuir isotherms for competitive adsorption and the respective adsorption constants K_{O_2}, K_{H_2O}. Here, it is assumed that only water and molecular oxygen competitively adsorb on the surface and all other gas phase constituents have negligible influence on the adsorption behavior.

$$y_{O_2} = \frac{K_{O_2} c_{O_2}}{K_{O_2} c_{O_2} + K_{H_2O} c_{H_2O} + 1} \quad (22)$$

Assuming that the respective reaction rates are linearly depen-dent on the surface coverage, the relative nitrate reduction rate f can then be calculated according to eqn (23). This equation also considers that the oxygen surface coverage decreases from its original value $y^0_{O_2}$ with increasing nitrate surface coverage due to the blocking of adsorption sites.

$$f = \frac{k_{NO_3} y_{NO_3}}{k_{NO_3} y_{NO_3} + k_{O_2} y^0_{O_2} (1 - y_{NO_3})} \quad (23)$$

For simplicity reasons, y_{NO_3} will be abbreviated as y and the oxygen contribution is simplyfied according to eqn (24), transforming eqn (23) into eqn (25):

$$k_0 = \frac{k_{O_2} y^0_{O_2}}{k_{NO_3}} \quad (24)$$

$$f = \frac{y}{y + k_0 - y k_0} \quad (25)$$

Now we will analyze the diff erent reaction pathways of the photogenerated holes and electrons. The following reaction rates are normalized for one reactive electron/hole-pair (molecules converted per reactive photon), assuming that for each oxidation also a reduction reduction must occur simultaneously and are dimensionless. In these equations, b is a figure for the amount of oxidation equivalents that are generated from each reduction of oxygen (0 to 3), as explained in the introduction. For each reactive photon, the amount of oxidation equivalents generated equals one (from the holes) plus up to three (from the electrons) which is further reduced if the electron reduces nitrate instead. In total this

$$b(1 - f)$$

equates to $1 + 4b$. To simplify things and also because it is not measured directly, HONO will not be considered as a viable reaction intermediate in the following. Instead, NO can either be oxidized to NO_2 before it is released, which takes 2 oxidation equivalents (eqn (26)), or to nitrate, which takes 3 oxidation equivalents (eqn (27)). The ratio between these two reaction pathways constitutes the initial or intrinsic selectivity of the material, S_0.

$$\text{rate}_{NO} = \text{NO} \cdot (1 - f) \cdot b \cdot \frac{1 - S_0}{2 + S_0} \quad (26)$$

$$\text{rate}_{NO} = \text{NO} \cdot (1 - f) \cdot b \cdot \frac{S_0}{2 + S_0} \quad (27)$$

$$\text{rate}(NO_3^- - NO_2) = f \quad (28)$$

The experimentally observed selectivity is the ratio between net nitrate formation and nitrogen monoxide oxidation, eqn (29), which can be rewritten using eqn (26)–(28), resulting in eqn (30).

$$S = \frac{\text{rate}(NO \rightarrow NO_3^-) - \text{rate}(NO_3^- \rightarrow NO_2)}{\text{rate}(NO \rightarrow NO_2) + \text{rate}(NO \rightarrow NO_3^-)} \quad (29)$$

$$S = S_0 - \frac{f (2 + S_0)}{4 - f} \cdot \frac{(4 - b)}{b} \quad (30)$$

with eqn (25) this finally becomes eqn (31).

$$S = S_0 - \frac{(2 + S_0)(4 - b)}{(y + 4)(y + k_0(1 - y) + y - b)} \quad (31)$$

As mentioned in the introduction part, the amount of oxidation equivalents generated through the reduction of oxygen (b) is likely not constant but will increase with lower reaction rate, e.g., when the nitrate coverage is higher and less electrons reach oxygen. Modeling this exactly is beyond this study, instead it will be approximated by using a simple exponential decay function with the parameter a, eqn (32), which transforms eqn (31) into eqn (18).

$$b = 3(1 - e^{-ay}) \quad (32)$$

$$S(y) = S_0 - \frac{(2 + S_0)(4 - 3(1 - e^{-ay}))}{(y + 4)(y + k_0(1 - y) + 3(1 - e^{-ay}))} \quad (18)$$

Conflicts of interest

There are no conflicts to declare.

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